

CHAPTER II

LITERATURE REVIEW

The present work is relating to the nanocomposite system of chitin-chitosan and other polymeric chains including some inorganic species. Hence, it is important to understand the properties of chitin-chitosan and also of shrimp and crab shell nanocomposites. It is also important to review the model cases of clay nanocomposites and other basic information on chitosan nanocomposite development.

2.1 Nanocomposite: Structures, Types, and Formation

Nanocomposite is a type of composites containing filler that has at least one dimension in the range of nanometer, i.e., a billionth of a meter. Most of the nanocomposites can be produced by using metal particles, colloids, and smectic-clay minerals. Nanotechnology has gained wide interest in the development of a novel polymeric composite, such as nylon 6-clay nanocomposites which were produced by Usuki *et al.* (1993). The polyimide-silica hybrid prepared by Mascia and Kioul (1995) is another example of polymer nanocomposites.

Dispersion of clay minerals in a polymer matrix is categorized into three types, i.e., conventional composite, intercalated nanocomposite and exfoliated nanocomposite as shown in Figure 2.1 (Pinnavaia *et al.*, 1996). **Conventional composite** contains the existing clay tactoids in original aggregated state with an unintercalated polymer chain along the silicate layers. The clay tactoids are simply dispersed as a segregate phase. **Intercalated nanocomposite** is formed by the insertion of one or more polymer chains into the clay galleries resulting in a well ordered multilayer with alternating polymer chains and nanoscale inorganic layers, owing to the spatial confinement of the polymer between the denser clay layers. Intercalated polymer-clay nanocomposites can exhibit improved conductivity. **Exfoliated nanocomposite** can be obtained by separating a single silicate layer in the polymer matrix with the average distance of each layer depending on the clay content. The clay contents in exfoliated nanocomposite are usually much lower than

in intercalated one. In addition, the undispersed hybrid corresponds to a conventional composite whereas the fine dispersed hybrid corresponds to either an intercalated or an exfoliated nanocomposite.

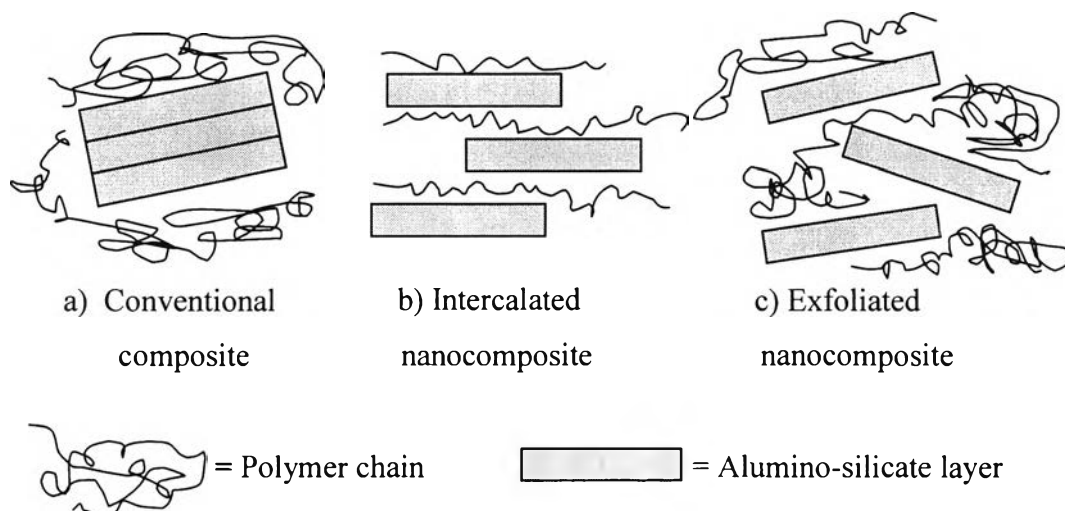


Figure 2.1 Three types of polymer-clay composites, a) conventional composite, b) intercalated nanocomposite, and c) exfoliated nanocomposite.

2.2 Silicate Clay Nanocomposite

Nanocomposite of silicate layers can be achieved with modified and non-modified silicate layers. Lemmon *et al.*, (1995) had prepared nanocomposite containing poly (ethylene oxide) with solid layer of Na-montmorillonite. Poly (ethylene oxide) and poly (ethyleneimine) were reported for composite materials with non-modified clay (Oriakhi *et al.*, 1996). In this case, silicate layers exhibit 3.9-4.7 Å lattice expansion along stacking direction. There are specific monomers that can be used as modifying agents for silicate layer. For example, monomers with amine group such as amine-terminated butadiene acrylonitrile has been used to produce butadiene acrylonitrile montmorillonite nanocomposite (Akelah *et al.*, 1994).

Most types of modified clay for nanocomposite are protonated organic compounds containing amine functional group. The modification with organic molecules of silicate layer improves the hybridization of silicate layers to polymer chains. Messermith *et al.* (1995) used organic modified silicate layers with 12-

aminododecanoic acid for preparation of nanocomposite of caprolactone. Content of silicate in the polymer matrix directly affected the molecular weight and size of crystalline of poly(caprolactone). The barrier properties to prevent water vapor transmission of poly(caprolactone) nanocomposite dramatically increased with small content of silicate layers. Various types of modified silicate layers were used with numerous kinds of polymers such as nylon 6 (Watari *et al.*, 1997), polyimide (Yano *et al.*, 1997), and epoxy (Pinnavaia *et al.*, 1996) to produce nanocomposite products. Zhang and Gonsalves (1995) prepared CaCO_3 -chitosan composites by dipping chitosan in a supersaturated CaCO_3 solution for the crystal growth of CaCO_3 on chitosan.

2.3 Chitin and Chitosan

Chitin-chitosan consists of glucopyranose ring with the functional groups of hydroxyl, amino and acetamide. Chitin-chitosan is known for its biocompatibility, nontoxicity and biodegradability. In nature, chitin is a copolymer between chitin and chitosan linked by a β -(1 \rightarrow 4)glycoside group with a high degree of N-acetylation (Muzzarelli *et al.*, 1977). In other words, chitosan (Figure 2.2) is a minor copolymer of N-deacetyl units in the chains, but it can be easily developed artificially from chitin by amination with the treatment of sodium hydroxide (Hirano *et al.*, 1989).

Production of chitin-chitosan from shrimp and crab shell as well as squid pens requires the steps of decalcification in hydrochloric acid and deproteination in sodium hydroxide solutions. The product is subsequently decolorized either by 0.5% potassium permanganate and oxalic acid or exposing to the sun light.

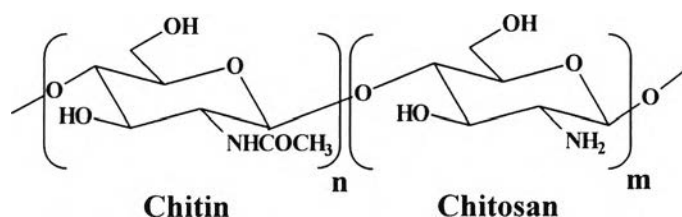


Figure 2.2 Chemical structure of chitin-chitosan.

It is important to note that the structure of crustacean shells can be defined as a type of intercalated nanocomposites. This natural bionanocomposite is an asset of chitin-chitosan, proteins and minerals. The most attractive point of this material is its superior physical and mechanical properties with complete biodegradability. Moreover, the network of hydrogen bonding of chitin-chitosan makes the material similar to a thermoset polymer.

In order to mimic crustacean shells, it is important to understand the chemistry and the induced specific properties from the molecular level. This will provide the approaches to design the artificial bio-nanocomposites based on the structure of chitin-chitosan hybridization with organic and inorganic materials.

2.4 Approaches for Chitin-Chitosan Nanocomposites

2.4.1 Chitosan-Clay Nanocomposites

Clay is a material appropriate for backbone layer composite because it provides the layer in nanoscale and helps to improve some physical properties. Clay or layered silicate is ubiquitous mineral as a component of soil. Clay is divided into groups according to their structure and layer charge such as talc, micas and smectites clay. Most of the clays are crystalline and composed of many repeating planes of oxygen anion holding together by the specific cations, such as aluminum and silicon ions described by Miller and Donahue (1990). The structure of a particular clay mineral is shown in Figure 2.3.

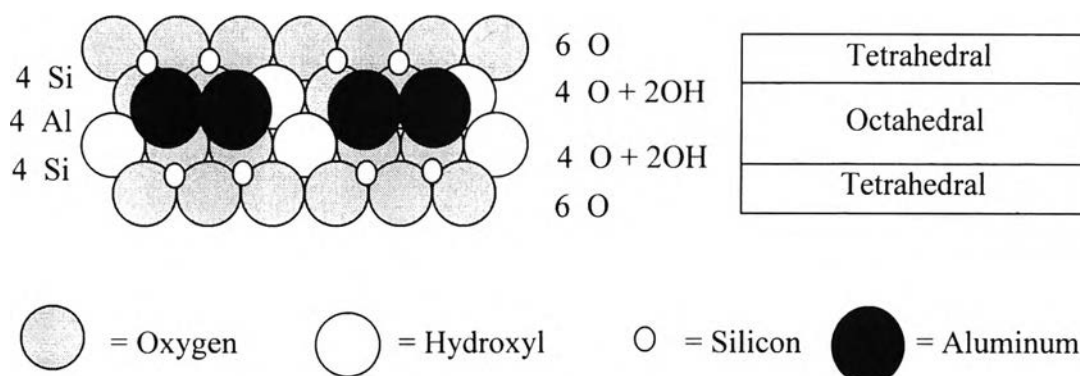


Figure 2.3 Two-dimensional model illustrating the arrangement of each component in a unit of clay mineral (Miller and Donahue (1990)).

Montmorillonite (MMT) is a group of smectic-clay minerals consisting of many layers of octahedral aluminate sheets sandwiched between tetrahedral silicate layers. Stacking of this structure leads to a regular weak dipolar or van der Waals interaction between the layers. Isomorphic substitution in each layer generates negative charges that are counterbalanced by hydrated sodium or potassium ions residing in the interlayer spaces. Due to this special characteristic, montmorillonite can be easily dispersed in water resulting in a stable colloid. The wide angle X-ray diffraction (WAXD) patterns show the basal spacing of MMT with various intercalation agents. The basal spacing of MMT can be increased by the organo-modification. For a certain type of intercalation agent, the basal spacing of organo-modified MMT increases with the chain length of the alkyl group.

Typically, the natural montmorillonite is difficult to disperse in an organic solvent. Its dispersibility can be improved by exchanging ion with an organic cation molecule, such as a cationic surfactant. The arrangement of smectic-clay structure by exchanging cation with a cationic surfactant is shown in Figure 2.4.

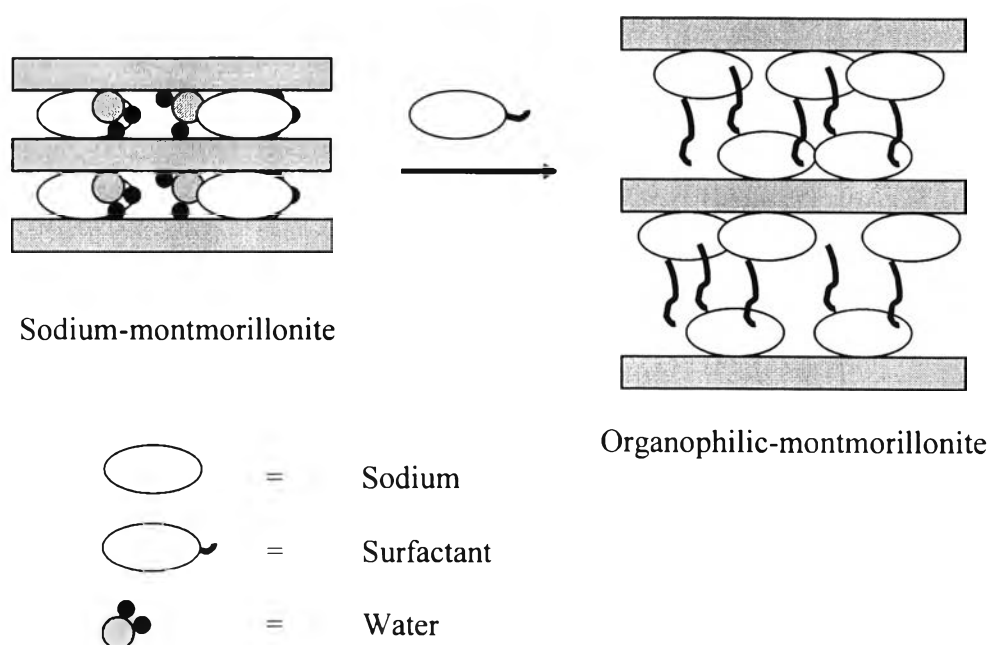


Figure 2.4 Arrangement of smectic-clay structure by cation exchange with a cationic surfactant (Lee and Kim (2002)).

The functions of organic cation molecules in organophilic-clay are to lower the surface free energy of the silicate layers and to improve the wettability behavior of hydrophobic polymer matrix. In addition, the organic cation may contain various functional groups that can react with the polymer molecules to improve the adhesion strength between the inorganic phase and the matrix as reported by Giannelis (1996).

As clay is a good material for nanocomposite formation, in this work, we pay attention to chitosan-clay nanocomposite.

Margarita *et al.* (2003) demonstrated the preparation of chitosan nanocomposite by using acetic acid to find that the clay layer was opened up from 1.20 to 2.09 nm under the feeding weight of 10 times chitosan to clay. Although the work showed the successful intercalation of chitosan into clay layer, the nanocomposite structure and the factors governing the intercalation process have not been reported.

2.4.2 Chitosan Nanocomposites

Chitin-chitosan shows strong inter-intra hydrogen bonds resulting in the problems of dissolution in water and organic solvents. This also brings chitin-chitosan to perform as thermosetting polymer even though structurally, it is a thermoplastic one. The packing structure of chitosan chain aligned in layer by layer to give the X-ray diffraction peak at 9° and $19^\circ 2\theta$.

In previous work, Margarita *et al.* (2003) demonstrated the preparation of chitosan nanocomposite by using Na^+ -montmorillonite as a main layer. The present work thus focuses on chitosan nanocomposite by applying chitosan as the main layer of intercalation.

2.5 Motivation of the Present work

Considering the supra-structure of crustacean shells and nanocomposites, we pay our attention to the development of artificial nanocomposites at molecular level by mimicking the natural structure of those shells. Here, chitin-chitosan is expected to provide a nanochannel to incorporate with other inorganic materials and/or polymer chains where the structure is well aligned either by ionic interaction

or hydrogen bonding as well as other secondary forces. In this work we aim to develop chitin-chitosan for biomimetic composite material.

Crab shell is a superb bionanocomposite material consisting of organic polymer chain of polysaccharide (chitin-chitosan) and protein while the inorganic minerals of calcium and magnesium are interpenetrating (Figure 2.5). Weiner *et al.* (2000) extracted proteins from mineralized crab shells and clarified the proteins that existed between the surfaces of the calcium carbonate crystals and chitin. In nature, the layer structure of chitin-chitosan and protein is hardened by binding with calcium and magnesium.

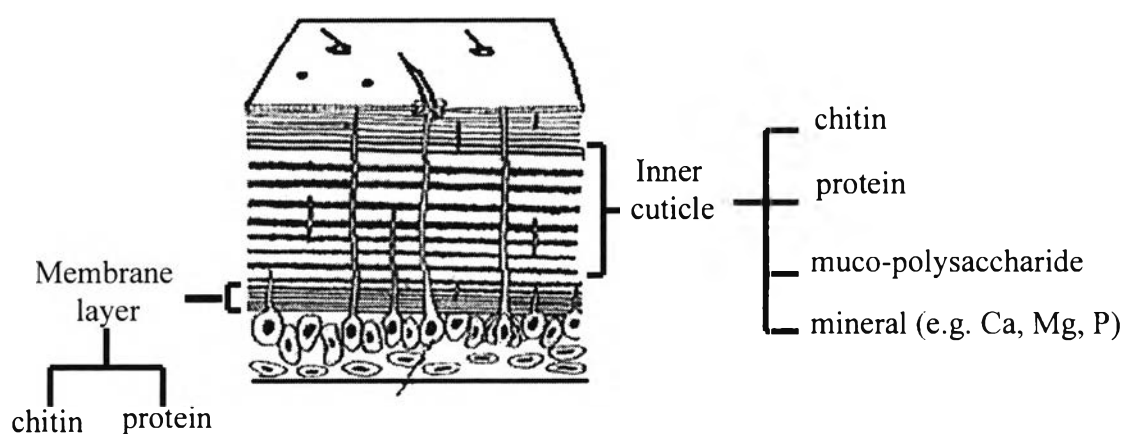


Figure 2.5 The structure of crab shell.

The present work pays attention to the layered structure of crab and shrimp shells in order to design chitosan chain layer polymers where we expect high adsorptivity with controlled hardening properties. It is a challenge to develop chitin-chitosan layer structure with synthetic polymer chain to mimic that of the crab and shrimp shell.